Ammonia Removal from Fly Ash by Carbon Burn-Out

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Carbon Burn-Out (CBO) combusts residual carbon in fly ash, producing a very consistent, low carbon, high-quality pozzolan. The process is continuous and is fueled solely by the residual carbon. Heat is recovered and sent back to the power plant that originally produced the high-carbon fly ash.

Progress Materials, Inc. has developed this technology, with support from EPRI and EPRI members. Extensive concrete testing has been done in order to demonstrate the superior characteristics of very low-carbon Class F fly ash from CBO. Carbon Burn-Out's ability to consistently produce high quality pozzolanic fly ash from numerous sources has been extensively documented. CBO fly ash has gained market acceptance and is regarded as a premium fly ash product in its market area.

Fly ash from pulverized coal power plants is a valuable mineral admixture in concrete. Its performance and economy have been well documented for several decades. Among other beneficial properties, fly ash enhances concrete's durability, especially its resistance to chemical attack. High-performance concrete combines high strength with long life, and is increasingly favored by life cycle costing. Fly ash is an important ingredient in this high value concrete.

Recently several utility ash managers have expressed concern about the ramifications from the increasing number of power plants injecting ammonia into coal fired generators. Coal fired power generation facilities are under increasing regulatory requirements for NO_x emission reductions. Recent United States EPA rule changes have resulted in coal fired utilities in states east of the Mississippi with the exception of Florida, Maine and Vermont be required to meet NO_x emissions of .15 lbs./ mmBTU.

In order to meet the new NO_x emission requirement, many utilities will use a combination of combustion management and post combustion processes. Combustion management techniques include low NO_x burners, over fired air systems, reburning and flue gas recirculation. The most commonly used combustion management technique is low NO_x burners. Low NO_x burners contribute to higher residual carbon levels in fly ash especially when operating for maximum NO_x removal. Post combustion processes include SCR selective catalytic reduction and SNCR selective non catalytic reduction.

Post combustion processes, SCR and SNCR use ammonia in the conversion reaction of NO_x to nitrogen and water. SCR normally uses a metal catalyst downstream of the economizer. SCR can accommodate different reaction temperatures depending on catalyst formulation. SCR systems have been successfully used in the 350°F to 1100°F temperature range.

SNCR ammonia injection occurs in the hot zones of the boiler and uses heat to drive NO_x reduction reactions. The NO_x reduction reaction will proceed at temperatures in the 1600°F to 2100°F zone. Both SCR and SNCR reduce NO_x by the following reactions:

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$
$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$

Post combustion NO_x controls result in a certain level of inefficiency in regards to the ammonia reducing process. This inefficiency results in fugitive ammonia emissions called ammonia slip. SCR systems typically operate with ammonia slip values in the five ppm range while SNCR systems operate considerably higher. Ammonia slip can be expected to vary widely depending on changes in operating conditions.

Ammonia slip results in a significant portion of ammonia being deposited on fly ash. European data indicates that combustion of coal in the 6–8 % ash range with slip values of 2 ppmv in the flue gas result in concentrations of approximately 100 ppmw of ammonia on fly ash. This example indicates that approximately one third of the ammonia slip reports to the fly ash.

Currently, little documentation exists as to the amount of ammonia residues found on fly ash resulting from NO_x reduction operations. It has been reported that low NO_x operations can produce ammonia concentrations in fly ash in the thousand ppm range.

NO_x control technologies will result in increased levels of carbon and ammonia found on fly ash. Carbon contents above 3% and ammonia concentrations above 100 ppm have been found to decrease fly ash market value. In fact, use of these technologies may result in once marketable fly ash becoming unusable and destined for disposal.

Ammonia contaminated fly ash will also result in re-evaluation of landfill disposal practices. Ammonia residues found on fly ash exhibit high water solubility and have the potential to contaminate both ground and suface waters.

Given the high probability of future fly ash sources containing increased carbon and ammonia, Progress Materials Inc. conducted an investigation as to ability of Carbon Burn-Out technology to simultaneously remove carbon and ammonia from fly ash.

Carbon Burn-Out has long been known as a very robust system for carbon removal for various types of ash feedstocks. Ash feedstocks containing carbon contents as high as 90% have been successfully processed. To date, over 200,000 tons of Carbon Burn-Out processed fly ash has been produced. CBO processed ash exhibits excellent pozzalanic activity, consistent air entrainment, carbon levels of 2 ½ % and has gained excellent market acceptance in it's market areas.

Carbon Burn-Out's fluid bed technology provides heat and residence time dictated by conditions for optimal combustion of carbon found in fly ash. Fly ash residence times of 45 minutes and temperatures in the 1300°F range are characteristic of the CBO process. Kinetic theory suggest that CBO conditions should be ideal for ammonia removal.

Ammonium Sulfate and Ammonium Bisulfate are the two prominent ammonia compounds found in coal fly ash. Both compounds exhibit low decomposition temperatures and should readily decompose within the operational conditions of Carbon Burn-Out.

In order to determine the effectiveness of ammonia removal by Carbon Burn-Out, several fly ash feed stocks of differing ammonia contents were processed. Processing was accomplished using Progress Material's one ton per hour pilot faciltiy located in Tampa, Florida. Fly ash was from a urea based SNCR fitted generating station. Fly ash of differing ammonia concentrations were processed.

Both feed and product samples were analyzed for ammonia content. Ammoniated fly ash was tested by several different methods. Testing methodology for ammonia in fly ash is not well defined. Presently no published methods for the determination of ammonia residues in fly ash exist. Well-defined methods have been used for solid matrices in the environmental testing industry. Environmental methods were selected for use in our testing program. Four methods were used ensuring method efficiency:

- EPA 350.2 uses aggressive acid distillation ensuring efficient ammonia recovery. A color-metric procedure is used for the determination of ammonia content.

- EPA 350.3 uses a less aggressive water dissolution for ammonia recovery. It is assumed that all ammonia complexes are highly soluble in water. A color-metric ammonia determination is used in this procedure.

- SM-4500C is a field technique designed for rapid determination of Ammonia during pilot plant operation. This method uses water dissolution followed by ammonia titration.

- The Boral procedure also provides a rapid field technique where the sample is treated by raising the pH and increasing sample temperature. The treatment results in the evolution of ammonia vapors, which are quantified by ammonia sensitive gas detector tubes.

Results indicate that under normal Carbon Burn-Out operating conditions essentially all ammonia was liberated from the fly ash feed material. Carbon Burn-Out successfully removed ammonia from feed ash containing ammonia at concentrations less than 1000 ppmw. **The Carbon Burn-Out process produced ash with less than five ppmw ammonia content for all feedstocks tested**.

Future work involves the determination of the fate of released ammonia in the flue gas. Results thus far concerning the fate of released ammonia are inconclusive. Two preliminary ammonia mass balance analyses indicate that 50 – 95% of the ammonia is being disassociated. Residence time and temperature inherent in the Carbon Burn-Out process should provide the necessary conditions for ammonia disassociation by the following reaction:

$2NH_3 \rightarrow N_2 + 3H_2$

Currently tests are being designed to determine the fate of the liberated ammonia.